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16. Abstract Gas-phase growth technologies for diamond synthesis are examined, which have led to wide applications as an important industrial material. The applications to be derived from new investigations are presented.					
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I. Introduction

Diamond, which is the most valuable gem in the world, is also very important for industrial materials. Because of its hardness, diamond is widely used for polishing and grinding materials. Beside its hardness, diamond has various superb properties for industrial materials such as antioxidation, good thermal conductivity, transparency for wide ranges of light (except ultrared), wide band gap, and making semiconductors with doping with impurity.

Natural diamond is produced very little and its production sites are limited to stable continents. For this reason, there have been a number of investigations on synthesis of diamond.

Natural diamond crystallizes at around 150 - 350km under the earth surface, and it bursts rapidly out on the earth surface with volcanic eruptions. Under normal atmospheric pressures, graphite is stable and diamond is quasi-stable. In order to synthesize diamonds, therefore, one has to generate temperatures and pressures as high as those at 150km under the earth's surface. With developing high pressure technology, a GE group in USA first synthesized artificial diamonds in 1955 using a metal solvent under a high temperature and pressure. This discovery opened a door to industrial materials of diamond. In recent days it is said that the amount of industrial usages of diamond is one index representing countries industrial standard. In 1986, Japan imported 30 million carats of diamond (93% of them are synthetic).

In recent years, basic technologies such as synthesis and processing of diamond have developed significantly; one can synthesize diamonds with control of their components and structures and use them with known properties. As a result, diamond becomes an important industrial material which is involved in

* Numbers in margin indicate pagination of foreign text.

the foremost advanced technology. Of these basic technologies, for the synthesis technology, the gas-phase growth technologies of diamond have been established. For this technology, Japan is the most advanced country in the world, and the number of investigators is increasing. The synthesized diamond by the gas-phase growth techniques is a thin film and thus more widely applicable to industrial usages than the traditional bulk diamonds. The diamond thin film increased its industrial usages. In Fig. 1, the basic technologies and diamond's applications are displayed. Of applications of thin film in Fig. 1, currently only speaker materials which utilize diamond's high sound velocity characteristics are in use. However, soon other applications will be realized.

156

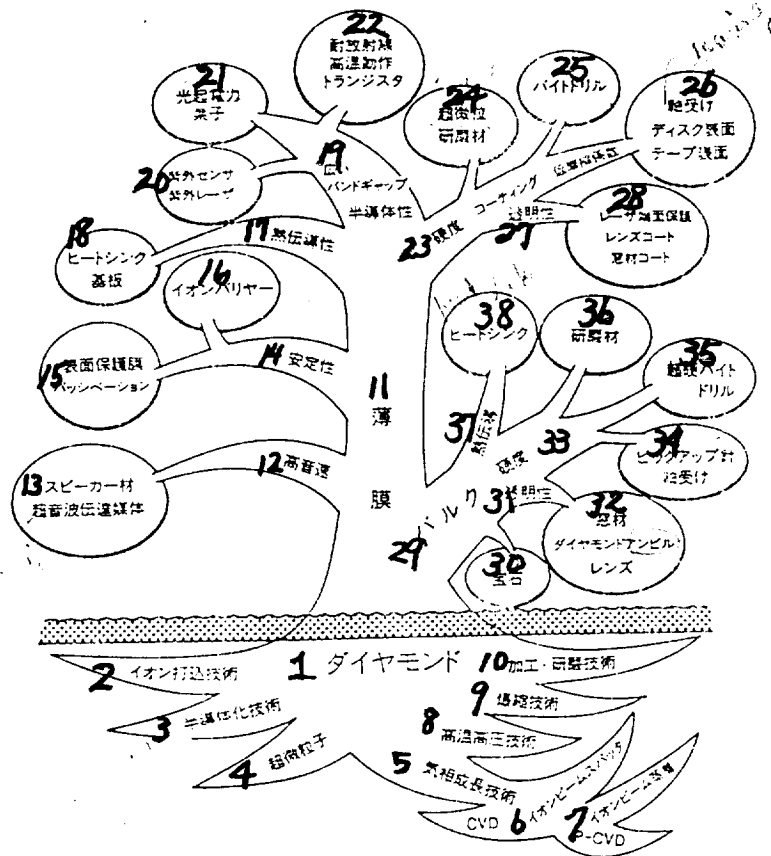
2. Gas-Phase Growth Techniques

The gas phase growth techniques of diamond thin film synthesis includes thermal filament CVD (chemical vapor deposition),¹⁻³⁾ plasma CVD,^{4,5)} ion beam vapor deposition,⁶⁾ ion beam sputtering deposition,^{7,8)} sputtering deposition^{9,10)}. The methods yield either self shaped crystal diamonds or diamond like carbon films (DLC film) which are amorphous but very hard.

157

The synthesis of diamond thin films is carried out under the reduced pressure where graphite is thermodynamically stable. Therefore, it is necessary to activate the process chemically or physically, otherwise only graphite is produced and no diamonds are obtained. The processes mentioned above for diamond synthesis are taken into account of such activation techniques. There are two activation techniques. One method is to chemically activate the process using hydrogens, and the other is to physically activate the process by colliding accelerated ions. The thermal filament CVD belongs to the former technique, while the ion beam vapor deposition and ion beam sputtering deposition to the latter one.

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Currently only thermal filament CVD and plasma CVD methods, which chemically activate the process, synthesize perfect diamond crystalline thin films without any amorphous structure. For this purpose the base board temperature should maintain more than 900°C. So far physical activation methods yield imperfectly crystallized diamond thin films, but it presents a possibility that crystalline diamonds can be synthesized at lower temperatures. In this review, we discuss the thermal filament CVD and ion beam sputtering techniques for chemical and physical activations, respectively. We also discuss the gas-phase growth techniques of diamond.

(a) Thermal filament CVD¹³

Fig. 2 displays the diagram of the thermal filament CVD for synthesizing diamond thin films. One of the characteristics of this apparatus is that the tungsten filament is right above the base board. During synthesis, the filament becomes more than 2,000°C. Carbons for diamond synthesis are taken from methane gas, which is diluted by hydrogen gas to yield 1 vol% of methane. Hydrogen gas molecules decompose with the heated filament which is more than 2,000°C, and become atomic hydrogens. The atomic hydrogens chemically activate the process.

The mechanisms of the chemical activation mentioned above may be as follows:

(1) Atomic hydrogens react with CH_4 and effectively yield radicals such as CH_3 , CH_2 , and CH . Resulting activated radicals decompose on the base board and generate diamond structures (Compared to the decomposition of CH_4 on the base board, that of radicals such as CH_3 proceeds at lower temperatures and films are formed effectively. It is also said that CH_3 radicals are important for forming diamond structures).

(2) Graphite-like carbons, which are produced simultaneously as diamonds are

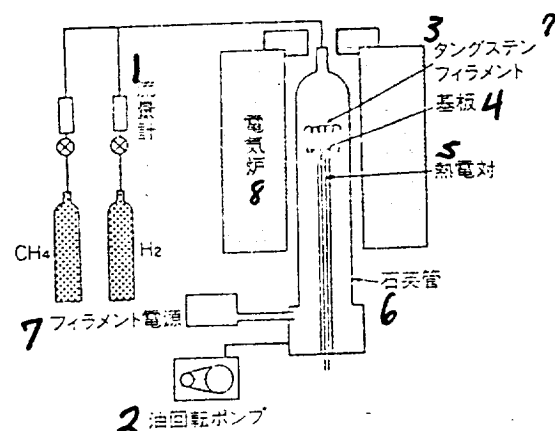


Fig. 2 Thermal Filament CVD Apparatus

1. flowmeter; 2. electric furnace; 3. tungsten filament; 4. base board; 5. thermo couple; 6. crystal tube; 7. filament electric source; 8. rotary oil pump.

produced, react with atomic hydrogens to yield hydrocarbons (Since in the phase domain for the synthesis graphite is stable, there is always a non-zero probability to produce graphites. Therefore, unless graphites formed are removed from the process, diamond crystals never grow. Graphites react with atomic hydrogens more easily than diamonds, and thus this technique selectively removes graphite-like carbons).

We obtained perfect crystalline diamond films on the base board which was maintained at about 900°C . On the base board diamonds form an epitaxial film. However, on the base board which is not diamonds but such as silicon, granules or diamond grow. In order to increase granule's yield, it is necessary to make scratches on the base board by diamond paste. Nuclei may be formed on the scratch, or diamond particles remain on the scratch and become nuclei for further

Fig. 3 Scanning Electron Microscope Photograph of a Diamond Crystal Thin Film

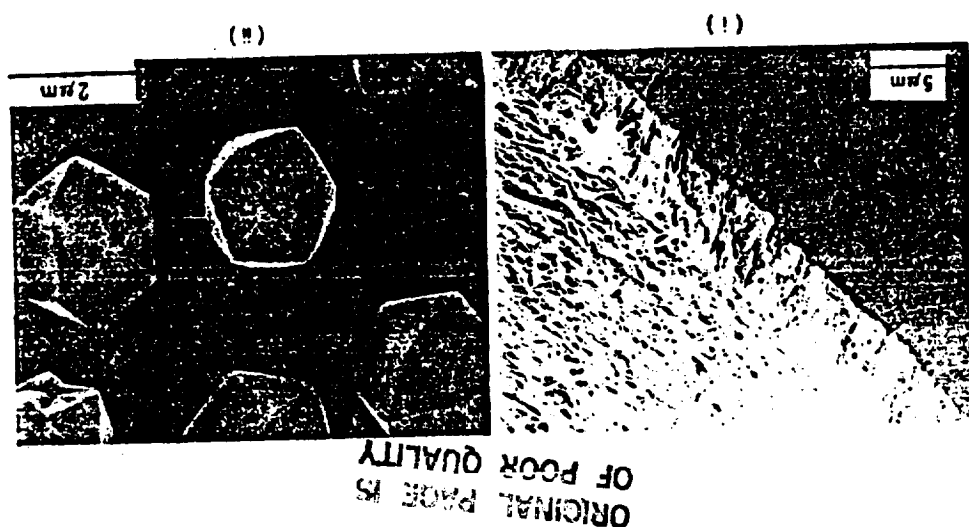


Fig. 3 (i) is a photograph taken by the scanning electron microscope (SEM)

of a diamond crystal thin film synthesized by the method mentioned above. Fig.

3 (ii) is that for granular diamond crystals. The thin film in (i) is an assembly of

granular diamond crystals and the surface of the film is not smooth. From Fig. 3

(iii) we find that the diamond crystal consists of (100) and (111) planes and that

there are many twin crystals. This indicates that the crystal growth occurred at

a relatively high supersaturated states. These results were reported by a group

of Inorganic Materials Institute. The same group also developed the microwave

plasma CVD method and obtained perfect diamond crystal thin films.

Recently various organic gases other than hydrocarbons are used; for example,

alcohols.¹² Steam was added or plasma states were altered.¹³ These modifications

increased the reaction speed. For example, it is now possible to crystallize 20

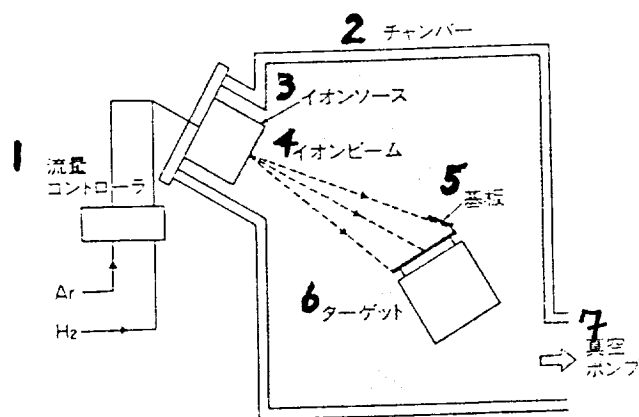


Fig. 4 Ion Beam Sputtering Deposition Apparatus

1. flow controller, 2. chamber, 3. ion source, 4. ion beam, 5. base board, 6. target, 7. vacuum pump.

(b) Ion Beam Sputtering Deposition⁹⁾

The ion beam sputtering deposition apparatus is schematically shown in Fig. 4. Mixed ion beams of argon and hydrogen, whose energies are about 1200 eV, are irradiated from the ion source. The target is a graphite sheet, from which carbon atoms are sputtered. Those carbon atoms are sources of diamond synthesis. The main feature of this apparatus is that the surface of the base board is nearly parallel to the ion beam at the irradiated position. Because of this orientation of the base board, high energy ion beams collide with the board surface and physically activate the process. This physical activation is considered to cause mainly heavy argon ion beams hitting a carbon film on the board surface. In more detail, the following interpretations are considered.

(1) A collision impact of ion beam on the base board locally forms high temperature and pressure domains and diamond synthesis starts there.

(2) The collision sputters carbon atoms in graphite-like structures whose bonding is rather weak, and removes amorphous structures.

In this process, hydrogen ion beams are also irradiated at the board surface. Thus, chemical activations mentioned in (a) may also exist. Such chemical activations as well as physical activations, whose effects are determined by the ion beam energy and irradiation angle, are optimized and superimposed, and thus diamonds grow at room temperature. Further, since the ion beam collides with the base board at a very shallow angle close to parallel to it, the temperature of the base board only slightly increases and maintains at room temperature. 160

Carbon films formed on the base board at room temperature are mostly amorphous and Vickers hardness of them is more than $3,000 \text{ kg/mm}^2$. These are DLC films. A photograph of a DLC film is shown in Fig. 5. This is taken by a transmission electron microscope. Granules are formed in the film. They are cubic diamond crystals, which consist of cubo-octahedral type cubic structures. The electron diffraction pattern and its shape reveal that the main planes are (100) and (111).

The ion beam sputtering method produces diamond crystals on the base board at room temperature. Several particles seen in the electron microscope view orient all in the same direction. However, these diamond particles are as small as $0.1 - 0.2 \mu\text{m}$. They are surrounded by amorphous structures and can not grow any further. For this reason, thin films of perfect diamond crystal can not be obtained, but DCL films whose surfaces are smooth are obtained. These can thus be applied to abrasion resistance films. Also since all particles orient to the same direction, heteroepitaxiality may be expected.

However, it is necessary to find a break through in order to yield perfect

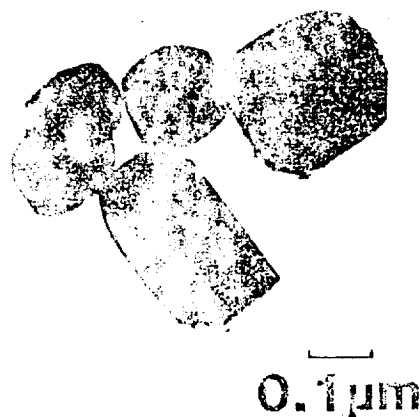


Fig. 5 Diamond Crystal Particles in a DLC Film.

diamond crystal thin films by removing all amorphous structures.

3. Evaluation of Diamond Thin Films

As mentioned above, carbon has two allotropes, graphite and diamond. Thus, identification of the diamond thin film should be carried out by at least two measurements. Structures, atomic vibrations, and electron states of the carbon thin film can identify diamonds.

Structure: the X ray and electron diffractions are used for structure analysis. One should be cautious since electron diffraction patterns of multicrystal diamonds are very similar to those multicrystal graphites. These are limited to crystals not for amorphous materials.

Atomic Vibration: The infrared absorption and Raman spectra reveal vibration frequencies of carbon or hydrogen atoms, which identify carbon atoms in a thin film are graphite-like (sp^2) or diamond-like (sp^3). Recently Raman scattering spectra produce most reliable data for diamonds.

Electron States: Energy loss spectra and Oje electron spectra yield electron

band structures in a thin film. This can distinguish diamond from graphite. Further one can obtain some knowledges of amorphous structures. DLC films often suggest mixed structures of diamond (sp^3) and amorphous carbon (sp^2).

These three factors indicate contents of crystals in the thin film. Impurities in the film should be identified similarly. For this purpose, the infrared spectra and the secondary ion mass analysis methods are used. These results together with physical properties (such as hardness, transparency, sound velocity) determine how diamond thin films should be synthesized. However, we have not evaluated in situ at the thin film formation. By developing this evaluation, we may solve a secret of diamond synthesis. 161

4 In Summary

We reviewed gas-phase growth technologies for diamond synthesis, which led to wide applications as an important industrial material. No one now complains about diamond synthesis using the gas-phase growth technology. However, no one knows how a diamond grows by this method. If one find the mechanism of diamond growth, one can develop various synthetic methods matching to their end usages. Inversely, new synthetic methods (for example, photo CVD¹⁵) may reveal the growth mechanism of diamond. New investigations will attain various applications shown in Fig. 1 and beyond.

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